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# Synthesis and Characterisation of Al<sup>3+</sup> and Cr<sup>3+</sup> Carboxyethyl Phosphonates and a Study of Their Ion Exchange Properties

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## ABSTRACT

New layered compounds of Aluminium (III) and Chromium (III) phosphonates, were synthesized by combining aqueous solution of M(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (M=Cr or Al) and aqueous solution of 3- phosphonopropionic Acid. The phosphonates were characterized by infra-red Spectroscopy. The IR Spectra of these compounds confirms the presence of major functional groups in these compounds. Ion Exchange of Aluminium and Chromium (III) phosphonates were also investigated using Potassium (K<sup>+</sup>) and Nickel Ni<sup>2+</sup>) and they proved to be good ion exchangers. The compounds were found to have the following stoichiometry: Al<sub>2</sub>(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>COOH)<sub>3</sub> and Cr<sub>2</sub>(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>COOH)<sub>3</sub>.

*Keywords:* Aluminium phosphonate; chromium phosphonate; layered compounds; ion exchange.

## DEFINITION

**XANES:** X-ray absorption near edge structure spectroscopy.

## 1. INTRODUCTION

Much interest is being devoted to organic –inorganic materials because of their high potentiality that they present for the design of materials with specific chemical or physical

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properties. The good stability of phosphorus oxygen metal bonds makes phosphonates especially interestingly for heterogeneous catalysts (Chaplais, et al., 2001). Metal phosphonate salts are hybrid organic/inorganic material in which the structure is directed by choice of metal and reaction conditions and the nature of the interlayer region depends on the organic moiety. Some work has been done in the synthesis of tetravalent metal phosphonates (Albert, et al., 1978; Alberti & Umberto 1974; Fuller, 1971; Alberti & Massucci 1970; Larsen and Gilley 1968) as well as divalent metal phosphonates (Cunningham & Hennelly, 1979). The crystal structure was assumed to be related to that of alpha zirconium phenylphosphonates  $Zr(O_3PC_6H_5)_2$ . The study of trivalent metal phosphonates has been done (Bujoli, et al., 1990). They have been extensively investigated as catalysts, sorbents and ion exchangers. The general interest in the chemistry of metal organophosphonates is mainly due to the unusual compositional and structural diversity varying from one dimensional arrangements to 3 dimensional microporous frame works passing by the most common layered networks (Clearfield and Stynes, 1964). The interest on synthesis of layered compounds arose after the realization that these compounds could be useful as exchange materials as there was a need for exchange materials with high degree of stability towards extreme temperatures and ionizing radiation and possessing appreciable exchange capacity over wide range of acidity (pH). The other importance is their applicability to research areas such as electrochemistry, microelectronics, biological membranes, petrochemical mechanisms and catalysts (Clearfield and Stynes, 1964). Cao, et al. (1990) prepared layered trivalent metal phosphonate salts  $MH(O_3PR)_2$  (R =alkyl, phenyl) (M= La, Sm, Co). They found  $LaH(O_3PCH_2)_2$  to be triclinic and the structure of  $MH(O_3PR)_2$  compounds to be closely related to that of other 1:2 layered metal phosphonate salts  $Ca(HO_3PC_nH_{2n+1})_2$  and  $M(O_3PR)_2$ . Raki and Detellier (1996) reported on the layered aluminium methylphosphonate  $AlOH(O_3PCH_3) \cdot H_2O$  and another aluminium phenylphosphonate was reported by Aranda et al., (1998)  $Al(HO_3PC_6H_5)(O_3PC_6H_5)_2 \cdot H_2O$  but its structure was not determined. Cabeza et al., (1998) synthesized six aluminium phosphonates with different conditions one structure was solved from powder diffraction data and  $^{27}Al$  and  $^{31}P$  MAS NMR and powder X-ray thermodiffractometric powder patterns for the aluminium phosphonates and their structure. Chaplais et al., (2001) synthesized aluminium phenylphosphonate,  $Al(OH)(O_3PC_6H_5)$  starting from aluminium nitrate and phenylphosphonic acid. They found the aluminium atom to be in a five co-ordination site based on its  $^{27}Al$  MAS NMR signal and on the XANES study. Such a site has not been reported in an aluminium phosphonate before. Barber et al., (2009) synthesized  $Ba^{2+}/Ti^{4+}$  metal phosphonate for high dielectric- polymer composite materials.

In this paper, we report the synthesis and characterization of two new carboxyphosphonates:  $Al_2(O_3PCH_2CH_2COOH)_3$  and  $Cr_2(O_3PCH_2CH_2COOH)_3$ . Their ion exchange capacity was also investigated using  $K^+$  and  $Ni^{2+}$ .

## 2. MATERIALS AND METHODS

### 2.1 Preparation of the Carboxyphosphonates

$M(NO_3)_3 \cdot 5H_2O$  (M=Cr or Al) 0.05 moles with aqueous solution of 3-phosphonopropionic acid ( $(OH)_2P(O)CH_2CH_2COOH$ ) (0.05 moles) were weighed on an analytical balance and dissolved in deionized water (100ml). The 3- Phosphonopropionic acid was dissolved in deionized water (50ml). The solutions were combined. In cases where precipitation did not occur upon combining the two, 0.1M aqueous solution of NaOH was added drop wise while the mixture was vigorously stirred. The resulting precipitate in its mother liquor was kept at 70 °C for several days in order to promote Oswald ripening of crystallites. The precipitate was

filtered, washed with water and ethanol and dried at 70°C air. The yield was measured and recorded.

## 2.2 Infrared Spectroscopy (FT-IR)

A FTIR 8101 Shimadzu was used. About 1-5% of the Phosphonate by weight in potassium bromide was ground into very fine particles. The mixtures obtained were pressed into transparent discs under a pressure of 8 tones. The discs were mounted on the instrument and the IR spectra obtained. The spectra of the ion exchanged phases were also obtained using the same procedure.

## 2.3 Ion Exchange Properties

### 2.3.1 K<sup>+</sup> exchange

The phosphonates (0.500g) were equilibrated with 100ml of 0.1M (KCl and KOH) solution for several days. The solids were filtered and IR Spectra obtained. The pH was measured and titrated with 0.010M HCl.

#### 2.3.1.1 Ni<sup>2+</sup> exchange

1g of each of the phosphonates was placed in contact with the following concentration of Ni<sup>2+</sup> 0, 0.2, 0.6, 0.8, 1.0 equivalents per gram (prepared from NiCl<sub>2</sub>.6H<sub>2</sub>O). Where 1 equivalent per gram equals  $2.25 \times 10^{-3}$  moles Ni<sup>2+</sup>. The pH of the solutions was measured. The IR spectra of the solids were obtained.

## 3. RESULTS AND DISCUSSION

Chromium phosphonate was found to be coloured, this is a characteristic of transition metal complexes.

Table 1. Physical appearance of the phosphonates

| Compound              | Description |
|-----------------------|-------------|
| Chromium phosphonate  | Green       |
| Aluminium phosphonate | yellow      |

### 3.1 IR Study

The Ligand IR spectra (table 2) show very broad peak in the 3000cm<sup>-1</sup> region, this is the OH stretch with hydrogen bonding due to P-OH and C-OH. The C=O stretch appears at 1716.9cm<sup>-1</sup>.

The complexes had peaks in the region 941.4 to 1142cm<sup>-1</sup>. This is the region typical for the phosphonate vibration (Clearfield, 1982). Bands in the region 375 to 600cm<sup>-1</sup> appeared and these are due to bending modes of the phosphonate groups. The range 1337 to 1485 cm<sup>-1</sup> and 2874 to 3000cm<sup>-1</sup> is for the alkyl groups (Yamanaka et al., 1979). The peaks were present in the complexes. The carbonyl stretch frequency is the region 1680 to 1725cm<sup>-1</sup> and for the complexes appeared at 1541.8cm<sup>-1</sup> which is within the range hence confirming the presence of this functional group. The carboxylic acid group is in the range 2500 to

3500cm<sup>-1</sup> (Clearfield and Smith 1968; Yamanaka et al., 1979; Dyer, 1965). In the spectra there appeared a broad peak confirming the presence of the carboxylic acid group.

**Table 2. IR data for (OH)<sub>2</sub>P(O)CH<sub>2</sub>CH<sub>2</sub>COOH**

| Peak/cm <sup>-1</sup>  | Description                  | Assignment                                   |
|------------------------|------------------------------|--|
| 2500-3600              | Strong, very broad           | O-H stretch (P-OH) ,(C-OH) with H- bonding   |
| 2900                   | Sharp, strong                | C-H stretch( saturated)                      |
| 1716                   | Moderately broad very strong | C=O stretch with H <sub>2</sub> O distortion |
| 1437.1                 | Very sharp peak              | P-C stretch                                  |
| 1269.3, 1211.4, 1018.5 | Sharp moderately strong      | P-O stretch (PO <sub>3</sub> )               |

Comparing the ligand IR spectra and the phosphonates, the peak due to the OH stretch narrows for the phosphonates this is probably due to the fact that the metals bonds the ligand through the PO<sub>3</sub> thus removing some OH groups. The OH stretch in the phosphonates spectra is from the carboxylic group. The C=O stretch is narrower in the phosphonates maybe due to the absence of water.

**Table 3. Titration volumes for K<sup>+</sup> exchange**

| Sample                | Average volume (ml) | Moles K <sup>+</sup> exchanged (M) |
|-----------------------|---------------------|------------------------------------|
| Chromium phosphonate  | 3                   | 3 X 10 <sup>-5</sup>               |
| Aluminium phosphonate | 2.7                 | 2.7 X 10                           |

**Table 4. Ion exchange for Ni<sup>2+</sup>**

| Ni <sup>2+</sup> exchange | pH of Cr solution | pH Al Solution |
|---------------------------|-------------------|----------------|
| 0                         | 4.06              | 4.79           |
| 0.2                       | 4.03              | 4.77           |
| 0.6                       | 3.99              | 4.75           |
| 0.8                       | 3.97              | 4.74           |
| 1.0                       | 3.87              | 4.72           |

For Ni<sup>2+</sup> exchange there is a general decrease in pH with increase in amount of Ni<sup>2+</sup> in contact with the compound. As the amount of Ni<sup>2+</sup> in solution increase more H<sup>+</sup> are displaced. The H<sup>+</sup> ions will move from the solid complex to the solution where they will cause a decrease in pH.

In the determination of the total exchange capacity the H<sup>+</sup> ion exchanged for M<sup>+</sup> ion reacts with OH<sup>-</sup> in solution. The remaining OH<sup>-</sup> that reacted and hence the amount of H<sup>+</sup> ions that were displaced by M<sup>+</sup>. The total exchange capacity of Aluminium phosphonate was 2.7 X 10<sup>-5</sup> moles.

### **3.1.1 Infrared spectra interpretation of exchanged phosphates**

The region 600- 800cm<sup>-1</sup> is for the coordinated water ( Cunningham & Hennelly 1979) their appearances in the spectra of the exchanged phases indicate the presence of coordinated

water. The >C=O stretch frequency has been reduced, this shows delocalization of electrons after bonding of the metal on the carboxylate end, however its appearance shows delocalization of electrons after bonding of the metal on the carboxylate end. Its appearance shows that there was incomplete ion exchange. Other peaks have already been discussed.

**Table 5. Infra-red spectra interpretation for Ni<sup>2+</sup> Exchanged Alumino phosphonate**

| Peak/cm <sup>-1</sup> | Description               | Assignment     |
|-----------------------|---------------------------|----------------|
| 418.6                 | Moderately broad and weak | P-O bends      |
| 1010.8                | Broad and weak            | P-O vibration  |
| 1093.8, 1197.8        | Moderately broad and weak | P-O stretch    |
| 1541.3, 1558.7        | Sharp and weak            | C=O stretching |
| 3560.8                | Sharp and strong          | O-H stretching |

**Table 6. Infra-red spectra interpretation for Ni<sup>2+</sup> Exchanged Chromium phosphonate**

| Peak/cm <sup>-1</sup> | Description                 | Assignment               |
|-----------------------|-----------------------------|--------------------------|
| 626.9                 | Sharp and moderately strong | P-O bending mode         |
| 1014.7                | Broad and strong            | P-O stretch              |
| 1201.8                | Moderately broad and strong | C=O stretch              |
| 1300                  | Strong                      | >CH <sub>2</sub> stretch |
| 1489.2                | Sharp and weak              | P-C stretch              |
| 1684.1                | Moderately broad and weak   | C=O stretch              |
| 2361.2                | Sharp and weak              | C-H stretch              |
| 3649.8                | Moderately broad and strong | O-H stretch              |

**Table 7. Infrared interpretation of Chromium complex exchanged with K<sup>+</sup>**

| Peak/cm <sup>-1</sup> | Description                | Assignment               |
|-----------------------|----------------------------|--------------------------|
| 526.6, 626.9          | Sharp and strong           | P-O bending mode         |
| 1012.8                | Sharp and strong           | P-O vibration            |
| 1095.7                | Sharp and strong           | P-O stretch              |
| 1201.8                | Sharp and strong           | C=O stretch              |
| 1300.2, 1385.1        | Sharp and weak             | >CH <sub>2</sub> stretch |
| 1541.3, 1558.7        | Sharp and weak             | C=O stretch              |
| 3649.8                | Sharp and moderately broad | O-H stretch              |

**Table 8. Infrared interpretation of Aluminium complex exchanged with K<sup>+</sup>**

| Peak/cm <sup>-1</sup> | Description                 | Assignment          |
|-----------------------|-----------------------------|---------------------|
| 418.6, 621.2          | Sharp and weak              | P-O bending         |
| 1008.9                | Broad and weak              | P-O vibration       |
| 1197.9                | Moderately broad and strong | P-O stretching mode |
| 1541, 1716            | Sharp and weak              | C=O stretch         |
| 3566.8                | Moderately broad and strong | O-H stretch         |

### **3.1.2 Ion exchange mechanism**

The layered structure of the phosphonate has layers which arrange themselves in such a way to create cavities between the layers. Largest entrance allows ions to diffuse into the

layers and be exchanged on the ion exchange sites available. Smaller ions can diffuse freely into layers without need for expansion of the layers. For larger ions the layers should be expanded and allow the ions to diffuse and ion exchange to occur. In this case layers should also be expanded, this can be done using OH<sup>-</sup> ions on intercalate amines.

At the surface of the crystal a hydrated ion gives up its water and enters the layer as an unhydrated or partially hydrated ion and exchange occurs without any need of expanding the layers and the exchange occurs at lower pHs.

This was found to be true for Ni<sup>2+</sup> exchange the pH measured were low for both complexes in the range 3.99-4.79. However in the case of K<sup>+</sup> this occurred at a pH of 8.08 for Chromium phosphonate. For main group aluminium phosphonate the exchange occurred at a pH of 5.2.

For K<sup>+</sup> in Chromium phosphate the high pH implies that K<sup>+</sup> is hydrated and there is need to expand the layers for exchange to take place. Hydroxide ions diffuse into the layers to the exchange sites and neutralize the protons. The accumulating negative charge would then force the layers apart so that the hydrated ions may enter and this occurs until all hydroxide ions have been consumed and the K<sup>+</sup> are exchanged. If pH remains high for a long period of time, the phase that is formed will have a high metal content and is stable at relatively high pH.

#### **4. CONCLUSION**

The new trivalent phosphonates, Aluminium and Chromium phosphonates can be synthesized by combining an aqueous solution of M(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (M=Cr or Al) with an aqueous solution of 2- carboxyethyl phosphoric acid which yield a green precipitate for Chromium and a yellow precipitate for Aluminium. The compounds have the following formulae Cr<sub>2</sub>(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>COOH)<sub>3</sub> and Al<sub>2</sub>(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>COOH)<sub>3</sub>.

Ion exchange capacities of Chromium and Aluminium for K<sup>+</sup> were found to be 3 X 10<sup>-5</sup> and 2.7 X 10<sup>-5</sup> m equiv/g respectively. The ion exchange for both complexes is via two phase. For both complexes i.e. Chromium and Aluminium the ion exchange was not complete as the carboxyl (C=O) peak on IR spectra did not completely disappear.

#### **ACKNOWLEDGEMENT**

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#### **COMPETING INTERESTS**

Authors have declared that no competing interests exist.

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APPENDIX

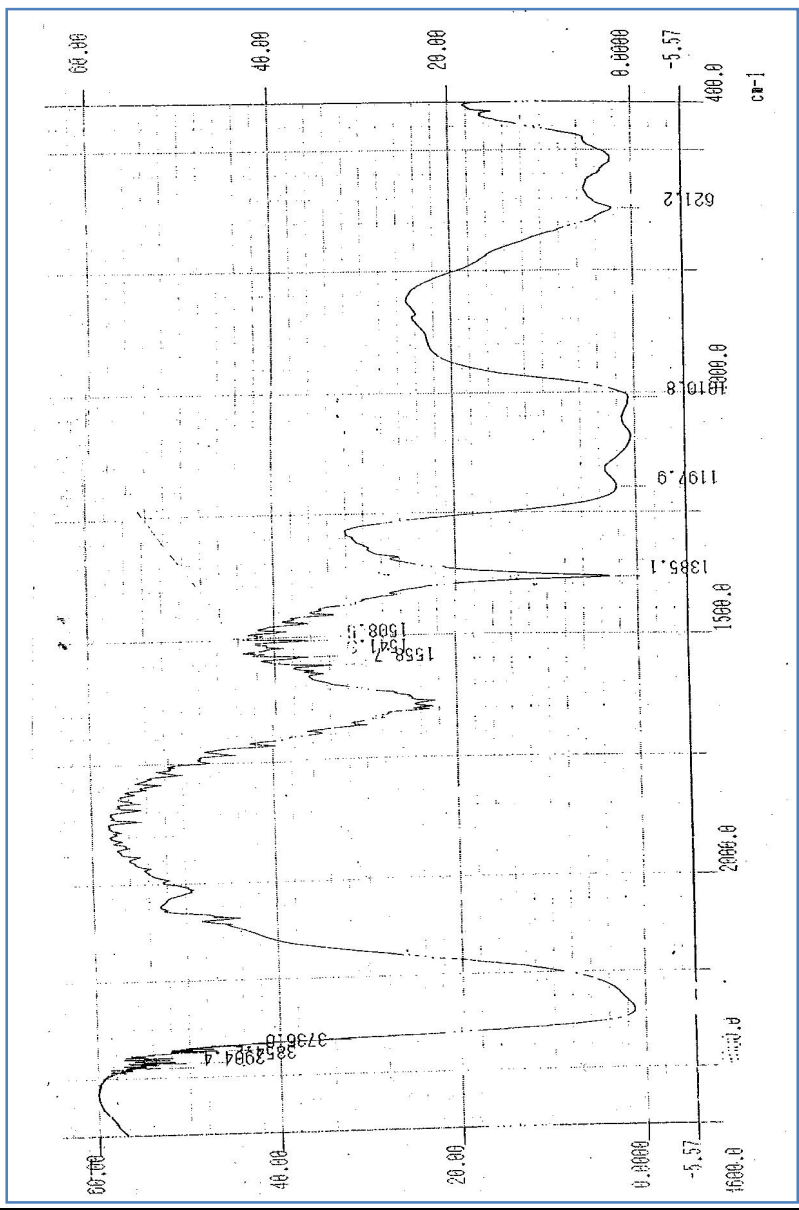


Figure 1: Infrared spectrum of Aluminium phosphonate



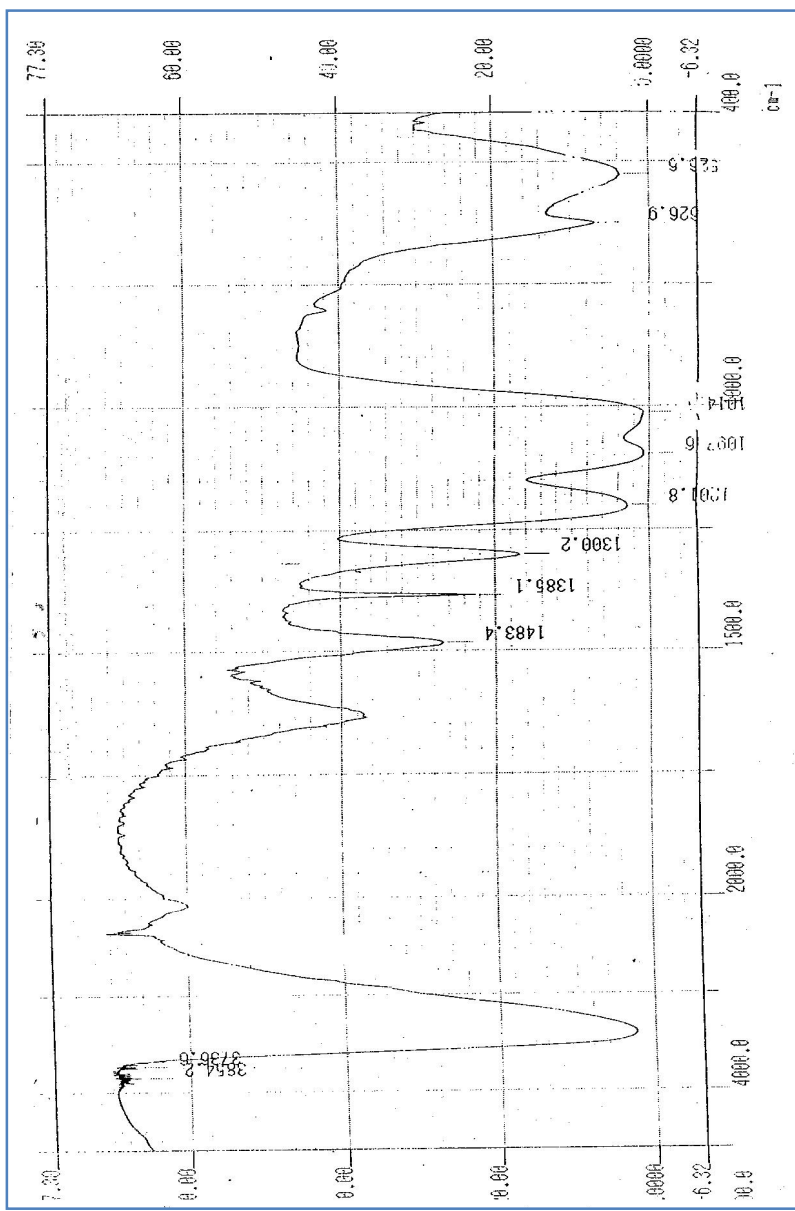


Figure 2: Infrared spectrum of Chromium phosphonate

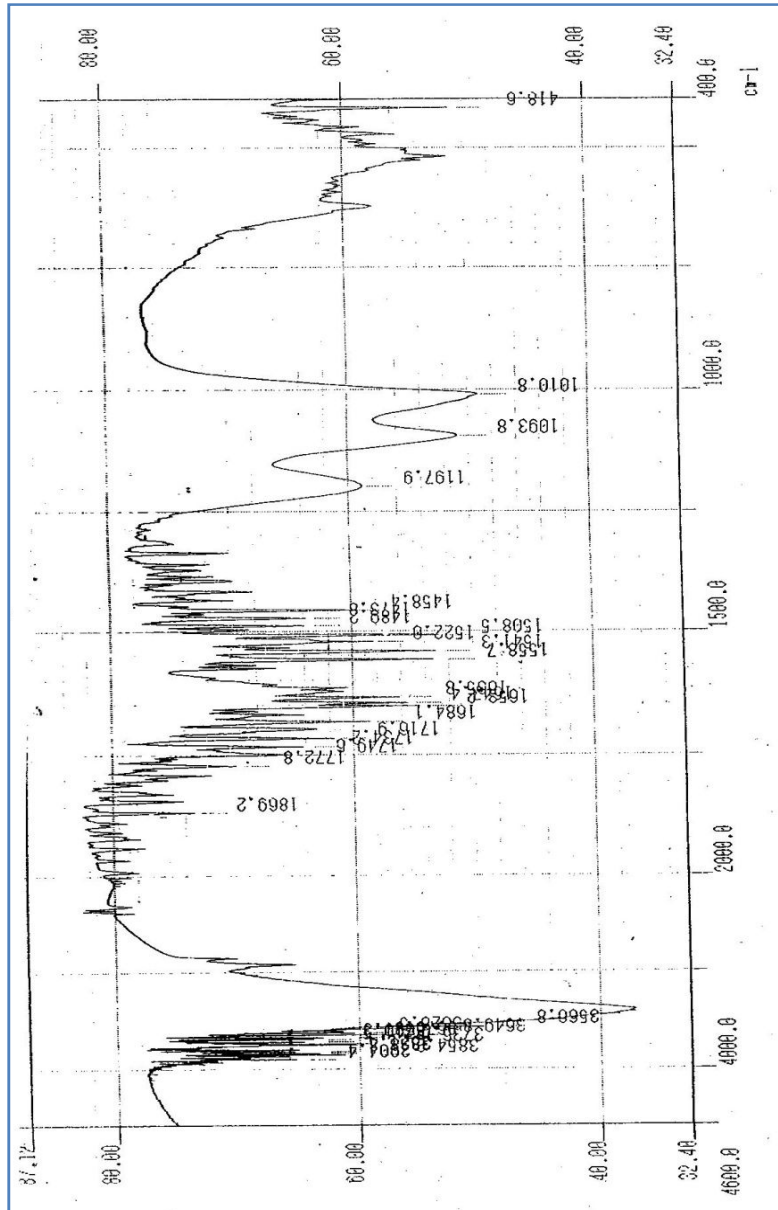


Figure 3: Infrared spectrum of Aluminium complex exchanged with Ni<sup>2+</sup>





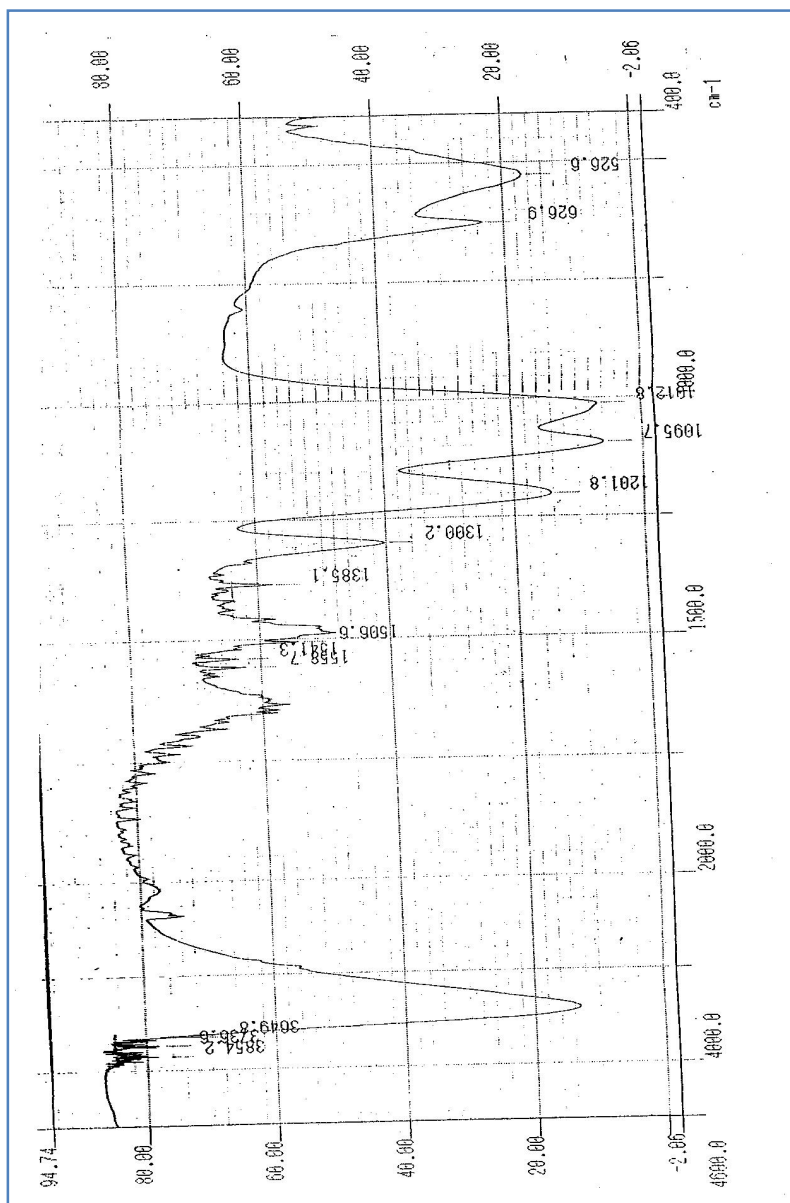
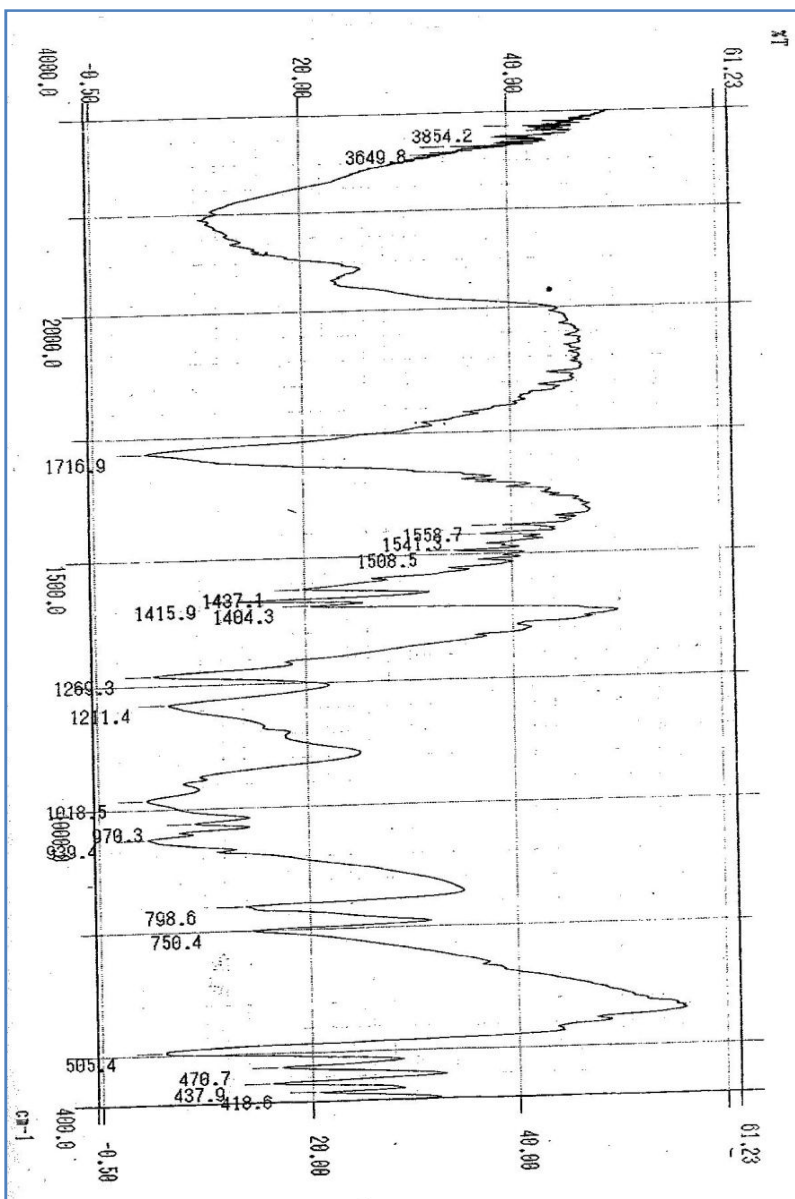


Figure 6: Infrared spectrum of Chromium complex exchanged with K<sup>+</sup>



**Figure 7: Infrared spectrum of carboxyethylphonic acid-the Ligand**

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